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On the thermal stability and nonisothermal decomposition kinetics of some lanthanum coordination compounds

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Abstract

The authors present their results concerning the thermal behaviour of two mononuclear and two polynuclear coordination compounds of lanthanum.

INTRODUCTION

Following our research concerning the thermal behaviour of rare earth coordination compounds [1], this paper deals with three *p*-aminosalicylate and one oxalate complex compounds of lanthanum.

EXPERIMENTAL

Powders of the following compounds: $[La(PAS)_2OH] \cdot 2H_2O$, $[Co(PAS)OH] \cdot 2H_2O$, $[LaCo(PAS)_3(OH)_2] \cdot 4H_2O$, $[LaCo(ox)_2OH(H_2O)_3] \cdot H_2O$, where PAS and ox are the *p*-aminosalicylate and oxalate anions, were used. The compounds were synthesised and analysed according to methods described elsewhere [2].

In order to obtain the heating curves, derivatographs from MOM-Budapest, of Paulik–Paulik–Erdey type with photographic recording (Q1500 D) and computer recording (Derivatograph C) were used. The TG, DTG, T and DTA curves were recorded in a static air atmosphere in the temperature range 20–1000 °C at heating rates (β) between 1.25 and 10 K min^{-1}.

The crystalline state of the powders submitted to heating was characterized by means of a TUR M62 X-ray diffractometer. The diffractograms were recorded using the $K\alpha$ radiation of cobalt. From the diffractometric data the mean sizes of the crystallites were evaluated using Scherrer's formula [3].

The nonisothermal kinetic parameter values were obtained using three integral methods: those of Coats and Redfern [4], Flynn and Wall for constant heating rate [5], and Urbanovici and Segal [6], which involves a modified Coats–Redfern method.

For automatic processing of the data a program written in the language BASIC was used [7]. Besides the optimal values of the nonisothermal kinetic parameters, this program regenerates, by using these values, the TG curves in coordinates (α, T), then the experimental points are recorded in the same coordinates.

Taking into account that the procedures applied to evaluate the nonisothermal kinetic parameters are based on various approximations of the temperature integral [8], the correspondence between the regenerated (α, t) curves (t = temperature, °C) and the experimental points indicates both the accuracy of the experimental measurements and the correctness of the description of the experimental data by these approximations.

RESULTS AND DISCUSSION

The thermal decomposition of $[La(PAS)_2OH] \cdot 2H_2O$

According to the derivatographic data, with progressive heating of this X-ray amorphous compound the following decomposition steps have been recorded:

$$[La(PAS)_2OH] \cdot 2H_2O(s) \xrightarrow{100-140\,^\circ C} [La(PAS)_2OH](s) + 2H_2O(g) \qquad (1)$$

$$[La(PAS)_2OH](s) \xrightarrow{150-200\,^\circ C} P(s) + P(g) + H_2O(g) \qquad (2)$$

where P(s) is the solid product of the decomposition and P(g) is the gaseous product of the partial degradation of PAS. Because of the lack of detailed information concerning the structure of the intermediate solid and gaseous products, the P_i notations are preferred.

$$P(s) \xrightarrow{200-300\,^\circ C} P_1(s) + P_1(g) \qquad (3)$$

$$P_1(s) \xrightarrow{700-800\,^\circ C} La_2O_3(s) + P_2(g) \qquad (4)$$

Table 1 lists the values of the nonisothermal kinetic parameters of reactions (1), (2) and (3). The results for these and for the following reactions were obtained from the data recorded at a fairly low heating rate in order to obtain values of the nonisothermal kinetic parameters free from heat transfer limitations.

The inspection of these results shows a satisfactory agreement among the values of the nonisothermal kinetic parameters obtained by means of the three applied methods.

Figure 1 shows the regenerated TG curve in (α, t) coordinates for reaction (2), recorded using the values of the Coats–Redfern nonisother-

TABLE 1

Values of the nonisothermal kinetic parameters for the decomposition of $[La(PAS)_2OH]\cdot 2H_2O$

Reaction number	β (K min^{-1})	Coats–Redfern method				Flynn–Wall method for constant β				Modified Coats–Redfern method			
		n	A (s^{-1})	E (cal mol^{-1})	r	n	A (s^{-1})	E (cal mol^{-1})	r	n	A (s^{-1})	E (cal mol^{-1})	r
1	3.12	0.9	2.29×10^{2}	8300	0.994	0.8	1.28×10^{3}	8900	0.995	0.8	2.26×10^{2}	8300	0.995
2	3.12	1.6	6.11×10^{10}	26100	0.998	1.6	9.82×10^{10}	26500	0.998	1.6	6.45×10^{10}	26100	0.998
3	3.12	1.5	2.27×10^{6}	21800	0.999	1.4	3.4×10^{6}	22000	0.999	1.4	1.8×10^{6}	21600	0.999

Key: n is the reaction order; r is the correlation coefficient for the linear regression.

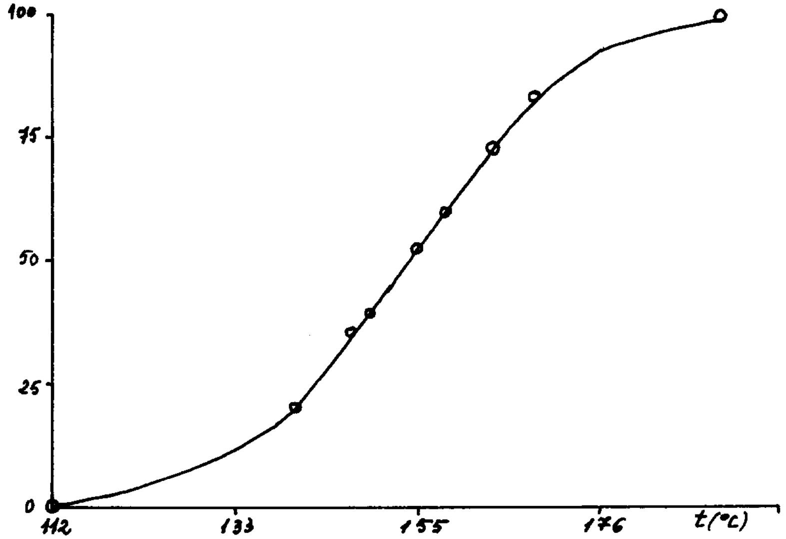

Fig. 1. The regenerated (α, t) curve and the experimental points for reaction (2): (———) regenerated curve; (○) experimental points.

mal kinetic parameters, as well as the experimental points which lie practically on the curve, thus indicating the validity of the applied method as well as the accuracy of the results.

The thermal decomposition of [Co(PAS)OH] · *2H₂O*

The derivatograms of this X-ray amorphous compound show the following decomposition steps:

$$[\mathrm{Co(PAS)OH}]\cdot 2\mathrm{H_2O(s)} \xrightarrow{100\text{–}120\,^\circ\mathrm{C}} [\mathrm{Co(PAS)OH}]\cdot \mathrm{H_2O(s)} + \mathrm{H_2O(g)} \tag{5}$$

$$[\mathrm{Co(PAS)OH}]\cdot \mathrm{H_2O(s)} \xrightarrow{180\text{–}200\,^\circ\mathrm{C}} \mathrm{P_2(s)} + \mathrm{P_3(g)} + \mathrm{H_2O(g)} \tag{6}$$

$$\mathrm{P_2(s)} \xrightarrow{630\text{–}640\,^\circ\mathrm{C}} \mathrm{Co_3O_4(s)} + \mathrm{P_4(g)} \tag{7}$$

$$\mathrm{Co_3O_4(s)} \xrightarrow{900\text{–}940\,^\circ\mathrm{C}} 3\mathrm{CoO(s)} + 0.5\mathrm{O_2(g)} \tag{8}$$

Only steps (5) and (6) are kinetically workable. The results are given in Table 2.

As can be seen from Table 2, the three integral methods applied to evaluate the nonisothermal kinetic parameters lead to results in satisfactory agreement.

The regenerated TG curve obtained using the Coats–Redfern nonisothermal kinetic parameter values, as well as the corresponding experimental points, are given in Fig. 2. In this case too, the experimental points fit well to the regenerated curve.

TABLE 2

Values of the nonisothermal kinetic parameters for the decomposition of $[Co(PAS)OH] \cdot 2H_2O$

Reaction number	β (K min^{-1})	Coats–Redfern method				Flynn–Wall method for constant β				Modified Coats–Redfern method			
		n	A (s^{-1})	E (cal mol^{-1})	r	n	A (s^{-1})	E (cal mol^{-1})	r	n	A (s^{-1})	E (cal mol^{-1})	r
5	2.85	2.1	1.31×10^7	15500	0.999	2.1	3.97×10^7	16000	0.999	2.1	1.44×10^7	15500	0.999
6	2.85	2.3	2.79×10^7	20600	0.999	2.3	7.81×10^7	21200	0.999	2.3	3.71×10^7	20800	0.999

Key: n is the reaction order; r is the correlation coefficient for the linear regression.

The thermal decomposition of $[LaCo(PAS)_3(OH)_2] \cdot 4H_2O$

The heating curves of this X-ray amorphous compound show the following decomposition steps:

$$[LaCo(PAS)_3(OH)_2] \cdot 4H_2O(s) \xrightarrow{120\text{–}140\,^\circ C} [LaCo(PAS)_3(OH)_2](s) + 4H_2O(g) \tag{9}$$

$$[LaCo(PAS)_3(OH)_2](s) \xrightarrow{180\text{–}200\,^\circ C} P_3(s) + P_5(g) + H_2O(g) \tag{10}$$

$$P_3(s) \xrightarrow{750\text{–}760\,^\circ C} LaCoO_3(s) + P_6(g) \tag{11}$$

The nonisothermal kinetic parameters values for reactions (9) and (10) are listed in Table 3. From an inspection of this table it is seen that the values of the nonisothermal kinetic parameters obtained by various methods show satisfactory agreement.

For reaction (9), Fig. 3 shows the regenerated TG curve as well as the experimental points.

The thermal decomposition of $[LaCo(ox)_2(OH)(H_2O)_3] \cdot H_2O$

The X-ray diffraction data of this compound are given in Table 4.

The derivatographic data allowed us to identify the following decomposition steps which occur with progressive heating of $[LaCo(ox)_2(OH)(H_2O)_3] \cdot H_2O$.

$$[LaCo(ox)_2(OH)(H_2O)_3] \cdot H_2O(s) \xrightarrow{130\,^\circ C} [LaCo(ox)_2(OH)(H_2O)_3](s) + H_2O(g) \tag{12}$$

$$[LaCo(ox)_2(OH)(H_2O)_3](s) \xrightarrow{225\,^\circ C} [LaCo(ox)_2(OH)](s) + 3H_2O(g) \tag{13}$$

$$[LaCo(ox)_2(OH)](s) \xrightarrow{300\,^\circ C} La_3Co_3(ox)_4O_{4.5}(s) + 0.5H_2O(g) + 3CO(g) + CO_2(g) \tag{14}$$

$$La_3Co_3(ox)_4O_{4.5}(s) \xrightarrow{345\,^\circ C} La_3Co_3(ox)_2(CO_3)_2O_{4.5}(s) + 2CO(g) \tag{15}$$

$$La_3Co_3(ox)_2(CO_3)_2O_{4.5}(s) \xrightarrow{400\,^\circ C} La_3Co_3(CO_3)_4O_{4.5}(s) + 2CO(g) + 2CO_2(g) \tag{16}$$

$$La_3Co_3(CO_3)_4O_{4.5}(s) \xrightarrow{480\,^\circ C} La_3Co_3(CO_3)_2O_{6.5}(s) + 2CO_2(g) \tag{17}$$

$$La_3Co_3(CO_3)_2O_{6.5}(s) \xrightarrow{760\,^\circ C} La_3Co_3O_{8.5}(s) + 2CO_2(g) \tag{18}$$

$$La_3Co_3O_{8.5}(s) \xrightarrow{930\,^\circ C} La_3Co_3O_{7.5}(s) + 0.5O_2(g) \tag{19}$$

The results concerning the nonisothermal kinetic parameter values of reactions (12), (13) and (18) (the reactions workable kinetically) are given in Table 5. A satisfactory agreement among the values of the nonisothermal

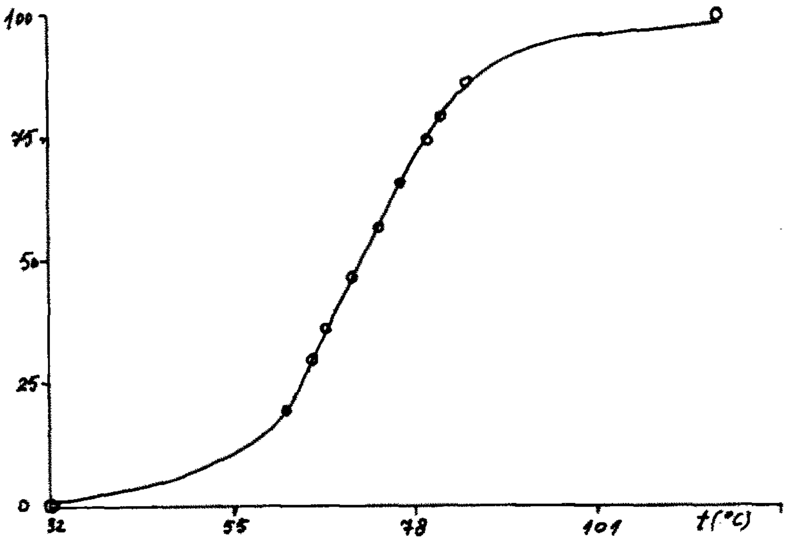

Fig. 2. The regenerated (α, t) curve and the experimental points for reaction (5): (———) regenerated curve; (o) experimental points.

kinetic parameters obtained by the three integral methods can be noticed in this case also.

The regenerated TG curve for reaction (12) and the corresponding experimental points are given in Fig. 4.

Examination of the results listed in Tables 1, 2, 3 and 5 shows that, with only one exception, the values of the reaction order are fractional and

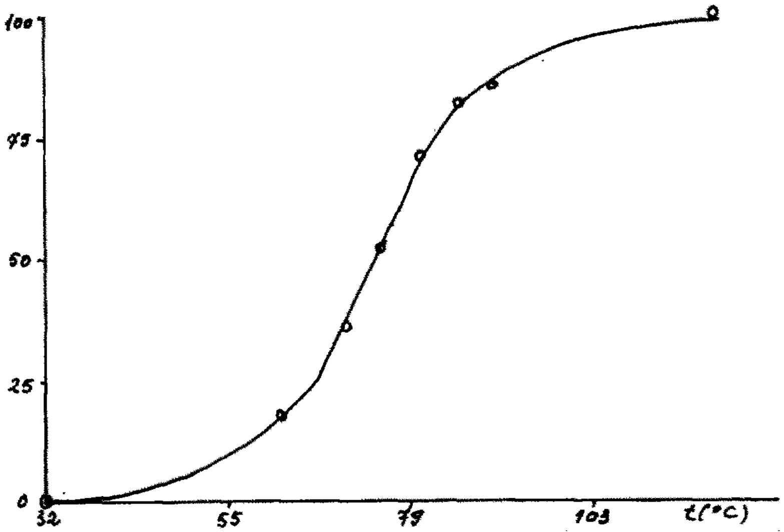

Fig. 3. The regenerated (α, t) curve and the experimental points for reaction (9): (———) regenerated curve; (o) experimental points.

TABLE 3

Values of the nonisothermal kinetic parameters for the decomposition of $[LaCo(PAS)_3(OH)_2]\cdot 4H_2O$

Reaction number	β (K min^{-1})	Coats–Redfern method				Flynn–Wall method for constant β				Modified Coats–Redfern method			
		n	A (s^{-1})	E (cal mol^{-1})	r	n	A (s^{-1})	E (cal mol^{-1})	r	n	A (s^{-1})	E (cal mol^{-1})	r
9	3.1	1.5	9.7×10^{8}	18800	0.996	1.4	3.15×10^{8}	18500	0.997	1.3	1.34×10^{8}	18400	0.996
10	2.85	1.9	9.9×10^{9}	25000	0.998	1.9	1.79×10^{10}	25500	0.998	1.8	8.2×10^{9}	24900	0.998

Key: n is the reaction order; r is the correlation coefficient for the linear regression.

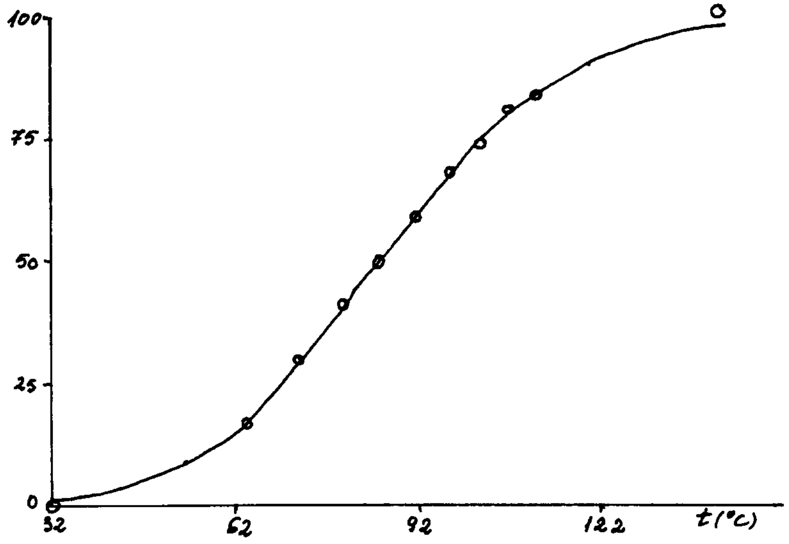

Fig. 4. The regenerated (α, t) curve and the experimental points for reaction (12): (———) regenerated curve; (o) experimental points.

higher than unity. These values could be assigned to the decomposition of structural units consisting of more than one molecule which coexist in variable ratios in the investigated systems.

TABLE 4

Intensity values corresponding to the X-ray diffraction lines, interplanar distances (d) and mean crystallite size corresponding to the most intense line (l) for $[LaCo(ox)_2(OH)(H_2O)_3] \cdot H_2O$

Number of diffraction line	Intensity	d (Å)	l (Å)
1	10.73	7.76	–
2	73.32	6.49	–
3	100	5.4	810
4	6.33	4.15	–
5	15	3.82	–
6	41	3.29	–
7	11	3.25	–
8	7	3.07	–
9	5	2.85	–
10	6	2.78	–
11	7.5	2.51	–
12	9	2.47	–
13	7	2.26	–

TABLE 5

Values of the nonisothermal kinetic parameters for the decomposition of $[LaCo(ox)_2(OH)(H_2O)_3]\cdot H_2O$

Reaction number	β (K min^{-1})	Coats–Redfern method				Flynn–Wall method for constant β				Modified Coats–Redfern method			
		n	A (s^{-1})	E (cal mol^{-1})	r	n	A (s^{-1})	E (cal mol^{-1})	r	n	A (s^{-1})	E (cal mol^{-1})	r
12	1.3	1.8	3.48×10^{3}	11100	0.998	1.7	1.2×10^{4}	11600	0.999	1.7	2.58×10^{3}	10900	0.999
13	1.25	3	2.22×10^{32}	73000	0.994	3	5.54×10^{31}	70900	0.994	3	–	–	–
18	4.8	1.2	3.43×10^{25}	126289	0.999	1.2	1.28×10^{25}	123761	0.999	1.2	3.79×10^{25}	126417	0.999

Key: n is the reaction order; r is the correlation coefficient for the linear regression.

CONCLUSIONS

The thermal behaviour of four coordination compounds of lanthanum was investigated.

The values of the nonisothermal kinetic parameters for the individual decomposition steps were determined.

The values of the nonisothermal kinetic parameters determined by three integral methods agree satisfactorily.

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